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PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN RELATING TO PREPARATION OF LITHOGRAPHIC ALUMINIUM PLATES"

COUNCIL OF OR SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1 India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

This is an invention by Shri Balkunje Anantha Shenoi, Scientist, Shri Ramachandar Subramanian, Scientist, Shri Srinivasan Chakrapani, Junior Scientific Assistant and Shri Ramasubbu Venkatachalam, Junior Scientific Assistant-all of the Central Electrochemical Resbach Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

The following specification describes the nature of this invention:—

This invention relates to improvements in or relating to the method of preparation of aluminium lithoplates.

Hitherto it has been proposed to use the mechanically grained zinc plates or aluminium plates (imported), or aluminium plates grained mechanically, chemically or electrochemically and/or subsequently anodised as claimed in our ealier Indian Patent No.96606.

This is open to the objection that the special zinc alloys of lithographic variety are imported and are comparatively costlier than aluminium and anodised aluminium lithoplates are also imported. Anodising of the aluminium plates as claimed in the Indian Patent No. 96606 employs an acid or acid mixture, which are toxic, corrosive and, though often adapted on large scale, their waste-disposal is a serious problem.

The object of this invention is to obviate these disadvantages by using a simple electrochemical technique for the preparation of aluminium lithoplates with properties suitable for lithographic purposes.

It is indicated in our earlier patent that the invention broadly consists in 'graining' the aluminium plates either (1) mechanically or (2) chemically or (3) electrochemically and/or (1) anodically treating the 'grained' plates in an aqueous solution containing fluorides, chromates, carbonates, phosphates of sodium, potassium and/or ammonium in concentrations not exceeding 15% by total weight of solids in solution, the current maintained by an applied voltage ranging from 10 to 200 volts DC or AC or superimposed AC over DC or (ii) suitably modifying the composition and operating conditions of the conventional anodising baths namely sulphric, chromic or oxalic or phosphoric acid baths or a combinations of these in appropriate proportions, and then making the film hyrophillic either by incorporating such substances ad dexritn, glucose, starch, dialdehyde starch, carboxy methyl cellulose with the anodising baths or in the subsequent sealing step.

Now it is found that after properly graining the aluminium plates as hereinoefore stated, subsequent anodising in a Borax sulution or Boric acid solution neutralised with an alkali to the desired pH range using either AC or DC in the following ranges gave desired oxide film for use as aluminium lithoplates:

Bath composition:	2–10% by weight of Borax in water
	2–5% boric acid neutralised
or	suitable alkali such as KOH, NaOH and/or NH_4OH
Temperature:	25°–40°C
Voltage:	20–30 volts across the electrode
Current applied:	AC or DC
Time:	15–30 minutes

When using DC, the work is made the anode in the circuit with lead, aluminium or steel as the cathode. When using AC, two plates are simultaneously anodised.

Use of Borax or Boric acid for the preparation of anodising bath has the following points in favour over the other anodising bath claimed in Indian Patent No. 96606 :

1. The electrolyte is non-toxic, non-corrosive
2. Waste disposal will not be a problem
3. Cost of the chemical is cheap and the chemical is readily available in India
4. The film obtained is as hard and abrasion-resistant as sulphuric acid anodised film.

The following typical examples are given to illustrate the present invention:

Example 1

Aluminium plates of above 99.5% purity conforming to the specification 2S or 3S are cleaned by immersion for one minute at 60°C in 10% sodium hydroxide solution, rinsed and then treated in 2% hydrochloric acid at 20V AC for 15 minutes at 40°C. The plates are then rinsed and treated anodically in the following electrolyte:

Borax crystals:	5% by weight in water
Temperature:	30°C
Voltage:	DC 30V
Anode:	The work
Cathode:	Aluminium plate
Time:	15 minutes

Rinse and dry.

Price : TWO RUPEES

EXAMPLE 2

After giving the treatments as detailed in Example 1 up to the anodising step, the two plates are electrolytically treated in the following solution at the given conditions:

Boric acid:	5% by weight in water
Ammonium hydroxide to adjust the pH to 10	
Temperature:	40°C
Voltage:	AC 20V
Electrodes:	Two grained plates
Time:	30 minutes

Rinse and dry.

In addition to the advantages claimed in our earlier patent (Indian Patent No. 96606), the following are the advantages of Borax anodising:

1. The borax electrolyte is cheaper than the other conventional anodising electrolytes. Where borax is not available as such, boric acid may be used as the starting material and may be neutralised with alkali. This solution is non-toxic and non-corrosive when compared with other conventional anodising electrolytes.
2. Waste disposal will not be a problem, as the electrolyte does not contain chromic acid or highly corrosive acids.
3. Storing of the chemical for the anodising bath is much more convenient than the other electrolytes like sulphuric acid, chromic acid and phosphoric acid.
4. Fume exhaust systems for anodising bath can be dispensed with.

Sd. Illegible
PATENTS OFFICER,
Council of Scientific and Industrial Research.

Dated this 23rd day of October 1970.

COMPLETE SPECIFICION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

THIS IS AN INVENTION BY SHRI BALKUNJE ANANTHA SHENOI, SCIENTIST, SHRI RAMACHANDAR SUBRAMANIAN, SCIENTIST, SHRI SRINIVASAN CHAKRAPANI, JUNIOR SCIENTIFIC ASSISTANT AND SHRI RAMASUBBU VENKATACHALAM, JUNIOR SCIENTIFIC ASSISTANT—ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, TAMIL NADU, INDIA, ALL INDIAN CITIZENS.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This invention relates to improvements in or relating to preparation of lithographic aluminium plates.

Hitherto it has been proposed to use mechanically grained zinc plates, imported aluminium lithoplates or aluminium plates processed according to the Indian Patent No. 96606. The imported lithographic quality zinc alloys are comparatively costly and their mechanical graining is done in a horizontal rocking machine with a slurry of fine abrassives and a number of marble balls for about an hour. Cost of such operation is around Rs 3/- per plate. The grains produced are not often uniform. The process is rather crude and time-consuming. Further, this process cannot be used for aluminium plates, because the plates after such a treatment tend to develop white spots. Further, the thin aluminium foils employed in Rotoprinting cannot withstand such a drastic mechanical treatment. Anodising of the aluminium plates as claimed in Patent No. 96606 employs an acid or acid mixture, which are toxic, corrosive and though often adopted on a large scale, their waste-disposal is a serious problem.

The object of the invention is to obviate these disadvantages by using a simple chemical or electrochemical technique for the preparation of aluminium lithoplates with properties suitable for printing and at the same time keeping an eye on the ease of operation economics and elegance of the process.

Another object of this invention is to prevent the defects due to atmospheric oxidation of the alumlnium surface and the development of white spots which makes the life of such plates short.

The present invention is based on the principle that the surface of an aluminium plate gets etched when treated chemically or electrochemically in solution containing alkali salts, chromates, phosphates, fluorides or their mixtures producing a uniformly grained surface. This is subsequently anodised using AC- DC or the combination in solutions of borax or boric acid neutralised with alkali to the required pH value and to the required concentration of the chemical.

According to the present invention, there is provided a process for the preparation of aluminium lithographic plates by cleaning the plates characterised in that the cleaned plates are subjected to chemical and/or electrolytic graining followed by anodising to provide an oxide film which hardens the grains.

The aluminium plate is grained by etching by treating chemically or electrochemically in solution containing alkali salts, chromates, phosphates, fluoride or their mixtures.

Carbonates, pyrophosphates, fluorides and bifluorides and chromates of ammonium, sodium or potassium and mineral acids like hydrochloric acid, nitric acid, hydrofluoric acid are used for chemical graining as a single electrolyte or as mixed electrolyte.

Chemical graining is carried out in a mixture of alkali chromate and carbonate or in a mixture of alkali pyrophosphate and fluoride or bifluorides of ammonia or potassium or sodium or in a solution of any of these acids, hydrochloric acid, hydrofluoric acid or nitric acid or in their mixtures.

The concentration of chemical graining solutions are used in the range of 1–10% w/v and/or v/v.

Chemical graining solutions are operated at temperatures ranging from 35°–60°C.

Electrochemical graining is carried in a solution of hydrochloric acid alone or in a mixture of hydrofluoric acid and nitric acid.

The electrochemical graining solutions are operated in the temperature range 25°–60°C.

Alternating current is used between the range 0 03 A/dm^2 and 0.1 A/dm^2.

The grained aluminium plate is subsequently anodised using AC, DC or the combination in solutions of borax or boric acid neutralised with alkali.

The anodising or oxidation is carried out in borax solution or ammonium, sodium or potassium salts of boric

acid in the voltage ranges 20 to 30V with AC or DC at 20 to 40°C.

The invention includes within its scope chemical compositions for chemical or electrochemical graining and subsequent anodising of aluminium plates for lithoprinting works comprising (a) carbonates, pyrophosphates, fluorides and bifluorides and chromates of ammonium, sodium or potassium and mineral acids like hydrochloric acid, nitric acid, hydrofluoric acid for chemical graining as a single electrolyte or as a mixed electrolyte and (b) borax or ammonium or sodium or potassium salts of boric acid for anodising as a single electrolyte.

Thus, a chemical and/or electrochemical process is provided for preparing an aluminium offset lithoplate comprising graining chemically or electrochemically. The subsequent oxidation of the surface improves the life of such grained plates.

By this process, the surface of the aluminium lithoplate is smoothly and uniformly grained to a controlled size and depth producing a porous structure. This makes a firm bonding with the photosensitive emulsions, say dichromated colloids, employed in printing. After subsequent developing in the usual way, the light hardened portions receive ink and the non-exposed areas being hydrophilic get dampened with sufficient water during printing. The impressions produced from such a surface are true to the original even in finer details. Thus, instead of other expensive planographic methods, after simple chemical and electrochemical treatment, aluminium plates can be used with improved results.

The electrochemical oxidation in a suitable electrolyte produces a film, waich apart from retaining the optimum grain size and porous structure to properly adsorb and retain ink and water in the respective areas, increases the mechanical hardness of the surface and resistance to corrosive atmospheres.

For preparing the aluminium plates according to this invention alloys of aluminium such as 2S, 3S, 65S and 57S can be provided the surface structure of aluminium plates is homogeneous and does not contain ony inclusions, i.e. free from surface defects.

The operation is performed as described hereunder. The aluminium plates supplied by the rolling mills are degreased to remove organic impurities by using a suitable organic solvent like trichloroethylene.

Then the plates are dip-cleaned at 25°C to 35°C in a 5 to 10% aqueous solution of sodium hydroxide for one to two minutes, rinsed in running water and chemically etched in any of the aqueous solutions given below:

(A)	Alkali chromate	—	1-4%
	Alkali carbonate	—	2-5%
	Temperature	—	60-100°C
	Time	—	2-5 minutes
	rinsed, followed by a dip in alkali or ammonium fluorides or acid fluorides	—	5-10%
	Temperature	—	35-50°C
	Time	—	1 minute
(B)	Hydrochloric acid	—	10-20%
	Temperature	—	30-35°C
	Time	—	2-3 minutes
(C)	Hydrofluoric acid	—	2-5% w/v
	Nitric acid	—	6.5-15% w/v
	Temperature	—	35-50°C
	Time	—	1-2 minutes
(D)	Alkali pyrophosphates	—	5-8% by weight
	Ammonium or alkali fluoride or bifluoride	—	1-2% by weight
	pH	—	2-3
	Temperature	—	30-35°C
	Time	—	5-12 minutes

Etching can also be performed in (B) or (C) by use of alternating current with two aluminium plates connected to the current leads into the electrolyte. The concentration of the chemicals may be varried within the following limits:

(E)	Hydrofluoric acid	—	0.1N-5N
	Temperature	—	30-50°C
	Current density	—	0.03-0.1 A/dm^2
(F)	Hydrofluoric acid	—	0.1-0.2% w/v
	Nitric acid	—	0 3-0.7% w/v
	Current density	--	0.03-0.1 A/dm^2
	Temperature	—	25-60°C

After treating in any of the above steps, the plates are thoroughly rinsed and treated chemically or electrochemically in the following solutions under suitable conditions. The plate is made anodic with a similar plate placed at a distance of 10-20 cm apart as the cathode.

(G)	Borax	—	2-10%
	or		
	Boric acid	—	2-5%
	(neutralised with a suitable alkali NaOH, KOH or or NH_4OH)		
	Temperature	—	20-40
	Voltage	—	20-30V across the electrodes
	Current applied	—	AC or DC
	Time	—	15-30 minutes

When using DC, the work is made the anode in the circuit with lead, aluminium or steel as the cathode. When using AC, two plates are simultaneously anodised.

After this electrolytic treatment, current is switched off, plates are removed, thoroughly rinsed in water and dried by warm air. The plates are now ready for further processing in the usual way for printing.

The time of treatment for one plate is about 40-45 minutes, if one plate alone is processed at a time in a tank. Depending on the capacity of the tank, the number of plates processed can be increased. Further, the process is also suitable for thin sheets of aluminium in the form of rolls and can be made continuous by proper design.

The following examples are given to illustrate the invention :

EXAMPLE 1

Degreased in trichloroethylene.

Dip-cleaned in 5% alkali solution at room temperature for five minutes.

Rinsed.

Chemically etched in aqueous solution containing :

Hydrofluoric acid	—	2% w/v
Nitric acid	—	6.5% w/v

At 40°C for 5 minutes

Rinsed.

Oxidation treatment in a solution containing :

Borax crystals:	—	5% by wt. in water
Temperature:	—	30°C
Voltage:	—	30V DC
Cathode:	—	Aluminium
Time	—	15 minutes

Rinsed and dried

EXAMPLE 2

Degreased in trichloroethylene.

Dip-cleaned in sodium hydroxide as above,

Electrochemically etched as follows:

Hydrochloric acid	—	0.2N–5N
Temperature:	—	20–50°C
Current density:	—	0.03–0.1 A/dm^2
Time:	—	15–25 minutes

Rinsed.

Oxidize in

Boric acid;	5% by wt. in water
Ammonium hydroxide; to adjust the pH 10	
Temperature:	40°C
Voltage;	20V AC
Electrodes:	2 grained plates
Time:	30 minutes

Rinsed and dried.

EXAMPLE 3

The plates are degreased and dip-cleaned as mentioned in the previous examples and chemically treated in the following solution :

Sodium chromate:	3%
Sodium carbonate:	5%
Temperature:	95°C
Time:	3 minutes

Rinsed. Given a whitening treatment in

Ammonium bifluoride:	10%
Temperature:	50°C
Time:	2 minutes

Rinsed· Finally anodised in a solution of borax as in Example 1 or 2.

EXAMPLE 4

Plates after degreasing and dip-cleaning as mentioned in Example 1 are treated chemically as follows :

Sodium pyrophosphate:	6%
Ammonium bifluoride:	2%
pH	3
Temperature:	35°C
Time:	6 minutes

Rinsed. Anodised in a solution of borax as mentioned in Example 1 or 2.

Following are among the main advantages of the invention :

1. The graining is more uniform when viewed under microscope and compared with plates prepared in other processes.
2. The grain size can be controlled to any desired limit
3. Number of impressions per plate is very high that it can be used for longer runs.

   A mechanically grained zinc plate gives about 20,000 impressions whereas the aluminium plates prepared by the processes according to this invention and the earlier invention (Patent N°. 96606) yield about 1,00,000 impressions for given method of plate-making say, gum process.

4. All the materials are readily available in India. All except pyrophosphate are manufactured in India.
5. The overail process is economical compared to th mechanical graining of zinc plates and manufacturing plates as per invention Patent No. 96606, The approximate cost of processing plates of same size in the above three processes is in the ratio of 20:8:7.
6. The anodising solution has the further advantages :

(a) it is non-toxic, non-corrosive

(b) waste disposal is not a problem

(c) the film obtained is as hard and abrasion-resistant as the film from sulphuric acid

(Hardness in Vickers No. a film from borax : 300–320
a film from H_2SO_4 : 250–300)

(d) corrosion resistance is greater than these films.
The plates anodised with borax or boric acid solution show no sign of corrosion even after 45 days of exposure to salt spary, while on plates anodised from sulphuric acid electrolytes corrosion spots can be seen even within 20 days of exposure,

(e) non-toxic fuming or spray.

We Claim :

1. A process for the preparation of lithographic plates by cleaning the plates characterised in that the cleaned plates are subjected to chemical and/or electrolytic graining followed by anodising to provide an oxide film which hardens the grains.
2. A process as claimed in Claim 1 where in the aluminium plate is grained by etching by treating chemically or electrochemically in solution containing alkali salts, chromates, phosphates, fluoride or their mixtures.
3. A process as claimed in Claim 1 or 2 where in the grained aluminium plate is subsequently anodised using AC, DC or the combination in solutions of borax or boric acid neutralised with alkali.
4. A process as claimed in any of the preceding claims wherein carbonates, pyrophosphates, fluorides and bifluorides and chromates of ammonium, sodium or potassium and mineral acids like hydrochloric acid, nitric acid, hydrofluoric acid are used for chemical graining as a single electrolyte or as a mixed electrolyte.
5. A process as claimed in any of the preceding claims wherein borax or ammonium or sodium or potassium salts of boric acid are used for anodising as a single electrolyte.
6. A process as claimed in any of the preceding claims wherein chemical graining is carried out in a mixture of alkali chromate and carbonate or in a mixture of alkali pyrophosphate and fluoride or bifluorides of ammonia or potassium or sodium or in a solution of any of these acids, hydrochloric acid, hydrofluoric acid or nitric acid or in their mixtures.
7. A process as claimed in any of the preceding claims where in the concentration of chemical graining solutions are used in the range of 1–10% w/v and/or v/v.
8. A process as claimed in any of the preceding claims wherein chemical graining solutions are operated at temperatures ranging from 35°–60°C.
9. A process as claimed in any of the preceding claims wherein electrochemical graining is carried in a solution of hydrochloric acid alone or in a mixture of hydrofluoric acid and nitric acid.
10. A process as claimed in claim 9 wherein the electrochemical graining solutions are operated in the temperature range 20–60°C.
11. A process as claimed in claim 9 or 10 wherein alternating current is used between the range 0.03 A/dm^2 and 0.1 A/dm^2.
12. A proces as claimed in any of the preceding claims wherein the anodising or oxidation is carried out in borax

solution or ammonium, sodium or potassium salts of boric acid in the voltage ranges 20 to 30V with AC at 20 to 40°C.

13. A process as claimed in any of the preceding claims wherein the aluminium plate is grained under conditions as claimed in claims 6 and 7 and then it is anodised under conditions as claimed in claim 12.

14. A process as claimed in any of the preceding claims wherein the plate is grained under conditions as claimed in claims 9 to 11 and then it is anodised under conditions as claimed in claim 12.

16. A process for the preparation of lithographic plates substantially as hereinbefore described.

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Deted this 13th day of July, 1971.

Capital Offset/Patent/73—150.